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PATENT SPECIFICATION

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(54) CROSS-LINKABLE COPOLYMERS

(71) We, WACKER-CHEMIE G.M.B.H., a body corporate organised according to the laws of the Federal Republic of Germany, of 8 München 22, Prinzregentenstrasse 22, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to cross-linkable copolymers of vinyl esters and/or of acrylic esters.

The cross-linking of polymers is often necessary so as to modify their properties according to the intended use of the polymers. They may, for example, be cross-linked so as to increase their resistance to organic solvents, to increase their resistance to water, to improve their mechanical resistance, or to reduce their thermoplasticity.

Various comonomers containing reactive groups are often incorporated into polymers so as to make the polymers cross-linkable. Such reactive groups are, for example, carboxy, hydroxy, amino, epoxy, N - methylol and substituted N - methylol (in which the hydrogen atom of the hydroxy group has been replaced by another atom or group) groups. Cross-linking can then be effected by reacting these polymers containing reactive groups with various poly-functional compounds. As a rule, however, the cross-linking of any particular type of copolymer can be effected only within a narrow pH range. German Auslegeschrift No. 1 249 524, for example, describes various copolymers of acryloylalkylaminotriazines, which can be cross-linked in an alkaline pH range.

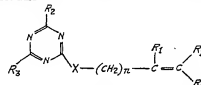
The present invention relates to copolymers of vinyl esters and/or acrylic esters, which can be cross-linked by acidic means, by basic means, or thermally.

The copolymers of the invention comprise

- (i) from 75 to 99% by weight, preferably from 90 to 99% by weight, of units derived from one or more monomers selected from

vinyl esters, acrylic esters, methacrylic esters, and, optionally, one or more other mono - olefinically or diolefinically unsaturated monomers (excepting those specified under components (ii) and (iii) below and excepting the functional comonomers mentioned below), provided that the weight of units derived from said other monomers does not exceed the weight of units derived from said ester monomers;

(ii) from 0.2 to 15% by weight, preferably from 0.5 to 5% by weight, of units derived from one or more olefinically unsaturated halogenotriazine derivatives of the general formula



in which each R₁ denotes a hydrogen atom or a methyl group, with preferably only one R₁ denoting a methyl group, R₂ denotes a bromine atom or, preferably, a chlorine atom, R₃ denotes a hydrogen or bromine atom, an alkyl group, or, preferably, a chlorine atom or hydroxy group, X denotes an oxygen or sulphur atom, or, preferably, an -NH- group, and n denotes 0, 1, 2 or 3, preferably 1 or 2; and

(iii) from 0.2 to 10% by weight, preferably from 0.5 to 8% by weight, of units derived from one or more mono - olefinically unsaturated monomers containing a free or protected N - methylol group;

all percentages being based on the total weight of components (i), (ii) and (iii).

Component (i) must include units derived from at least one vinyl ester, acrylic ester or methacrylic ester. The vinyl esters may be esters of any straight or branched carboxylic acid, advantageously having up to 18 carbon atoms. Preferably, the vinyl ester is of a carboxylic acid having 2, 3 or 4 carbon atoms, optionally in admixture with one of a

carboxylic acid having from 8 to 18 carbon atoms. The acrylic and methacrylic esters may be of any primary or secondary alcohol, advantageously having up to 18 carbon atoms.

- 5 Preferably, the acrylic or methacrylic ester is of a primary or secondary alcohol having up to 8 carbon atoms, optionally in admixture with up to 35 mole % of an ester of a longer-chain alcohol. Mixtures of two or more vinyl esters and/or acrylic esters and/or methacrylic esters can be used.

Examples of suitable vinyl esters are vinyl formate, acetate, propionate, butyrate, hexanoate, 2 - ethylhexanoate, laurate, and versate ("Versatic acid" is a trade mark).

- 15 Examples of suitable acrylic and methacrylic esters are those of methanol, ethanol, propanol, butanol, 2 - ethylhexanol, cyclohexanol, and lauryl alcohol.

- 20 Component (i) may optionally include units derived from one or more other mono - olefinically or diolefinically unsaturated copolymerisable monomers. The amount of these other units present should not exceed more than 50% by weight, preferably not more than 30% by weight, of the total amount of component (i).

- Examples of these other olefinically unsaturated monomers are vinyl halides, for example, vinyl chloride or fluoride; vinylidene halides, for example, vinylidene chloride or fluoride; vinyl aromatic compounds, for example, styrene, methylstyrene, vinyltoluene, and vinylpyridine; vinylpyrrolidone; esters of α,β - unsaturated monocarboxylic or dicarboxylic acids having from 4 to 10 carbon atoms with alcohols having up to 18 carbon atoms, for example an ester of an acid selected from crotonic, isocrotonic, maleic, fumaric and itaconic acids with an alcohol selected from methanol, ethanol, propanol, butanol, and mixtures thereof, or from 2 - ethylhexanol, cyclohexanol, lauryl alcohol, and mixtures thereof, or from mixtures of the short-chain esters with up to 35 mole % of the long-chain esters; olefins, for example, ethylene, propylene, and butylene; conjugated diolefins, for example, butadiene, isoprene, and 2,3 - dimethylbutadiene; and acrylonitrile.

The units in component (ii) are derived from olefinically unsaturated halogenotriazine derivatives. Examples of suitable derivatives are:

- 55 2 - allylamino - 4,6 - dichloro - s - triazine,
2 - allylamino - 4 - chloro - 6 - hydroxy - s - triazine,
2 - allylamino - 4 - chloro - 6 - ethyl - s - triazine,
60 2 - allylamino - 4 - chloro - 6 - propyl - s - triazine,
2 - allyloxy - 4,6 - dichloro - s - triazine,
2 - n - butenyloxy - 4,6 - dichloro - s - triazine,

- 2 - isopentenylloxy - 4,6 - dichloro - s - triazine, and
2 - allylthio - 4,6 - dichloro - s - triazine.

The triazine derivatives may be prepared, for example, as described in *Recueil 78 (1959)* pages 967 ff, and in *Makromolekulare Chemie 81 (1965)* pages 129-136.

Component (iii) comprises units derived from one or more mono - olefinically unsaturated monomers containing one or more free or protected N - methylol groups. Examples of such monomers having free N - methylol groups are N - methylolacrylamide, N - methylolmethacrylamide, and N - methylolallylcarbamate. Examples of protected N - methylol groups, which give free N - methylol groups during cross-linking, are N - methylol alkyl ether groups, N - methylol ester groups, and Mannich bases.

It can be advantageous for the copolymers additionally to comprise units derived from one or more functional comonomers. Such units may be present in amounts of from 0.5 to 10% by weight, preferably from 1 to 5% by weight, relative to the total weight of components (i), (ii) and (iii). The term "functional comonomers" means an unsaturated monomer containing one or more atoms or groups selected from hydroxy groups, epoxy groups, reactive halogen atoms, carboxylate groups, carbamoyl groups, sulphonate groups, and amino ester groups, for example, an α,β - unsaturated carboxylic acid (for example, acrylic, methacrylic, maleic and fumaric acids); an α,β - unsaturated carboxylic acid amide (for example, acrylamide and methacrylamide); hydroxyethylacrylate, hydroxyethylmethacrylate, hydroxybutylacrylate; glycidylacrylate, glycidylmethacrylate; α - hydroxypropylacrylate, 3 - chloro - 2 - hydroxypropylacrylate; 1,2 - oxypropylacrylate; a sulphonic acid derivative of an olefinic compound, for example, sodium vinyl sulphonate; a monoester and diester of an α,β - unsaturated monocarboxylic acid with an amino alcohol, for example, dimethylaminoethylacrylate.

It can also be advantageous to include triallyl cyanurate or diallyl phosphate, preferably in an amount of from 0.05 to 0.5% by weight, relative to the total weight of components (i), (ii) and (iii).

The manufacture of the copolymers of the invention can be carried out by conventional methods, for example, by bulk, solution, precipitation, suspension, or, preferably, emulsion polymerisation. Polymerisation may be carried out in the presence of a polymerisation initiator and, optionally, a dispersion auxiliary and other auxiliaries, at a temperature of from 0 to 100°C, preferably from 40 to 80°C. It is advantageously carried out under the autogenous pressure of the monomers. In the case of gaseous monomers, pressures of

up to 100 atmospheres gauge may be used, preferably of up to 40 atmospheres gauge.

The polymerisation initiators used are free-radical initiators. Suitable initiators are, for example, inorganic and organic peroxy compounds and certain azo compounds. They may be used in amounts of from 0.01 to 5% by weight, preferably from 0.1 to 3% by weight, relative to the total weight of monomers.

Examples of suitable peroxy compounds are acyl peroxides, for example, benzoyl or acetyl peroxide; ketone peroxides, for example, methyl ethyl ketone peroxide; peresters, for example, *t*-butylperpivalate; alkyl hydroperoxides, for example, *t*-butyl hydroperoxide and cumene hydroperoxide; and inorganic peroxides, for example, hydrogen peroxide, and sodium, potassium, or ammonium peroxydisulphate. A suitable azo compound is, for example, azobisisobutyronitrile.

The initiators may be used in conjunction with reducing agents as redox polymers, in known manner. The reducing agents may be used in amounts of from 0.01 to 5% by weight, preferably from 0.1 to 3% by weight, relative to the total weight of monomers.

Examples of suitable reducing agents are sodium sulphite, sodium bisulphite, sodium formaldehyde sulphonylate, hydrazine, triethanolamine, sulphinic acids, hydrogen in combination with a noble metal sol, preferably a palladium sol, and heavy metal salts, for example, iron, copper, or cobalt sulphate.

Molecular weight regulators, for example, aldehydes, organic halogen compounds, mercaptans, and nitro compounds, can be used in the polymerisation medium to control the molecular weight in a conventional manner.

Solvents in which the monomers are soluble are suitable for polymerisations using solvents. Such solvents are, for example, chloroform, ketones, e.g. acetone, ethyl acetate, tetrahydrofuran, and dioxane. Precipitation polymerisation can be carried out using, for example, methanol as the solvent. Suspension polymerisation can be carried out in water or in an aliphatic hydrocarbon as the suspension medium, optionally with the addition of suspension stabilisers and buffer substances.

The preferred method of manufacturing the copolymers of the invention is by emulsion polymerisation in the presence of an emulsifier and/or a protective colloid, a free-radical initiator, and, optionally, one or more other auxiliaries. Suitable dispersions having a solids content of up to 65% by weight can be prepared in this manner.

The protective colloids are suitably used in amounts of from 0.3 to 3% by weight, relative to the total weight of monomers. Suitable protective colloids are, for example, wholly or partially saponified polyvinyl

acetates having an acetate content of from 20 to 60 mole %, preferably from 35 to 45 mole %; water-soluble cellulose derivatives, for example, carboxymethylcellulose, carboxypropylcellulose, hydroxyethylcellulose, and hydroxypropylcellulose; polyvinylpyrrolidone; polyacrylic acids; polyacrylamides; and water-soluble acrylic acid/acrylamide copolymers.

The emulsifiers may be either non-ionic or anionic, or mixtures thereof. Anionic emulsifiers are suitably used in amounts of from 0.05 to 3% by weight, relative to the total weight of monomers. Non-ionic emulsifiers are suitably used in amounts of from 0.3 to 6% by weight, preferably from 1 to 3% by weight, calculated on the total weight of the dispersion (including liquid and solid components).

Examples of suitable anionic emulsifiers are alkylsulphonates, alkarylsulphonates, alkylsulphates, hydroxyalkylsulphates, alkyl- and alkaryl- disulphonates, sulphonated fatty acids, sulphates and phosphates of alkyl- and alkaryl- polyethoxyalkanols, and sulpho-succinic acid esters. Examples of suitable non-ionic emulsifiers are addition products of from 5 to 50 moles of ethylene oxide and/or propylene oxide per mole of straight or branched alkanols having 6 to 22 carbon atoms, alkylphenols, carboxylic acids, carboxylic acid amides, primary and secondary amines and also block polymers of ethylene oxide and/or propylene oxide.

Free-radical initiators that are particularly suitable for use in emulsion polymerisation are water-soluble peroxy compounds, for example, peroxydisulphates, hydrogen peroxide, and *t*-butyl peroxide, optionally together with the reducing agents mentioned above.

Polymerisation can be carried out with all of the monomers being initially introduced into the polymerisation medium, for example, an aqueous emulsion. Alternatively, one or more of the monomers can be wholly or partially metered in, continually or in doses, during the course of the polymerisation.

The copolymers can be manufactured in such a manner that there is no substantial cross-linking. The non-cross-linked copolymers are soluble in a variety of solvents, for example, chlorinated hydrocarbons, dioxane, tetrahydrofuran, toluene, ethyl acetate and butyl acetate.

Cross-linking of the copolymers can be effected thermally by brief heating to a temperature of from 100 to 150°C, preferably from 130 to 150°C. Alternatively, cross-linking can be effected at a pH below 3 by the use of an acid catalyst or at a pH above 9 by the use of a basic catalyst. The use of a catalyst can be combined with thermal cross-linking.

Suitable acid catalysts are, for example, mineral acids, e.g. dilute hydrochloric or

sulphuric acid; organic acids, e.g. formic, acetic, oxalic, tartaric, and p - toluene sulphonic acids; and salts that hydrolyse to give acids in aqueous solution, e.g. aluminium chloride, ammonium chloride, and zinc nitrate. Suitable basic catalysts are, for example, ammonium hydroxide, sodium hydroxide, calcium hydroxide, and primary, secondary and tertiary bifunctional or polyfunctional amines, e.g. triethanolamine, triethylamine, diethylenetriamine, and hexamethylenediamine.

Copolymers of the invention can be applied in the form of aqueous solutions or, preferably, as aqueous dispersions, for a variety of purposes in the field of binders and coating agents, as they have an improved resistance to water and to solvents, an improved mechanical strength, and a reduced surface tackiness. They are particularly suitable as binders for paints, adhesives, fleeces, joint fillers, printing inks, and paper-coating compositions. They are compatible with commonly used auxiliaries, such as pigments, fillers, and plasticisers. They can also be used to modify the adhesive strength and mechanical properties of hydraulically setting substances, such as cement, plaster, and lime.

The following examples illustrate the invention; parts and percentages are by weight.

Example 1

Preparation of 2 - allylamino - 4,6 - dichloro - s - triazine.

18.5 parts of cyanuric chloride were dissolved in 100 parts of acetone and added, while stirring, to a mixture of 300 parts of water, and 400 parts of crushed ice. The suspension thus obtained was added to 5.7 parts of allylamine over a period of 30 minutes and subsequently to an aqueous solution of 5.3 parts of sodium carbonate. The white crystalline reaction product was suction-filtered, washed several times with iced water, and dried over phosphorus pentoxide.

Copolymerisation.

400 ml of water, 31 g of nonylphenol etherified with 20 moles of ethylene oxide per mole of nonylphenol, 1 g of a sodium alkylarylsulphonate, 3 g of sodium vinyl sulphate, and 0.4 g of potassium peroxydisulphate were placed in a 2 litre round-bottomed flask fitted with a reflux condenser, stirrer, metering device, nitrogen inlet and a heatable, and coolable jacket. After rinsing with nitrogen, 107 g of the monomer solution comprising 530 g of vinyl acetate and 6 g of allylaminochlorotriazine were added to the flask contents and the reaction medium was heated to 65°C. Polymerisation was initiated by the addition of 10 ml of a solution of 1 g of sodium formaldehyde sulphonylate in 40 ml of water, and the remainder was added to the solution in portions over a

period of 3 hours. Once the polymerisation had started, the remaining vinyl acetate solution, a solution of 5 g of acrylic acid, 5 g of acrylamide, and 30 g of N - methylolacrylamide, together with a solution of 2.0 g of potassium peroxydisulphate and 1 ml of concentrated ammonia in 60 ml of water, were added to the reaction mixture over a period of 2 hours.

After all additions had been made, polymerisation was continued for a further 30 minutes at 65°C, and then the mixture was cooled. A stable coagulate-free dispersion (of average particle size) was obtained, which was adjusted with water to a solids content of 50%, and which then had a viscosity of 600 cP (measured with the Epprecht-Rheometer stage III). The pH of the dispersion was 4.5. Two samples were taken from the dispersion: one was adjusted to a pH of 2 with 5N HCl and the other to a pH of 10 using 5N NaOH. Both from the original dispersion and from the acid and alkaline samples, a 0.2 mm thick film was poured out, and the degree of cross-linking and the swelling index of the untempered film and of the films after tempering at 150°C for 2 minutes were determined in the manner described below.

(a) Degree of Cross-linking.

Approximately 500 mg (G_1) of the air-dried dispersion film were boiled in a 300 ml Erlenmeyer flask, with ground stopper equipped with a reflux condenser, in 50 ml of ethyl acetate for 6 hours under reflux. The residue contained in 20 ml of the clear solution was determined after evaporating the solvent and drying at 110°C to constant weight (G_2). The degree of cross-linking DC was calculated as follows:

$$DC = 100 - (250 \cdot G_2) / G_1, \%$$

(b) Swelling Index.

50 ml of ethyl acetate were introduced, using a pipette, into a 300 ml Erlenmeyer flask with a ground stopper. A 15 mm wide and 30 mm long strip of the air-dried film of the dispersion having a weight of 100 to 200 mg (G) was placed in the solvent for 24 hours and the whole was shaken occasionally. The swollen film was then dried with parchment paper and was immediately introduced into a weighed weighing glass having a ground lid (W_1), which was then re-weighed (W_2), 20 ml of the solution were put into a beaker which has been weighed exactly and contained boiling stones (B_1), and this was reweighed (B_2) after the solvent had evaporated and after the residue has been dried at 110°C to constant weight. The swelling index was calculated according to the following formula:

$$S = \frac{W_2 - W_1}{G - (B_1 - B_2) \cdot 2.5}$$

The results are tabulated below:

5	Untempered film			
	pH	2	4.5	10
	DC	77	0	75
10	Tempered film			
	pH	2	4.5	10
	DC	92	90	87
	S	2.0	2.6	2.5

Example 2

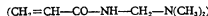
345 ml of water, 24 g of a partially saponified polyvinyl alcohol having a hydrolysis degree of 90%, and 2 g of nonylphenol etherified with 23 moles of ethylene oxide per mole of nonylphenol, were introduced into the apparatus described in Example 1. After rinsing with nitrogen, 115 g of a monomer solution consisting of 455 g of vinyl acetate, 6 g of 2-allyloxy-4,6-dichloro-s-s-triazine (prepared in known manner according to *Makromolekulare Chemie* 81 (1965) pages 129-136), and 2 g of 6-butyl hydroperoxide, were added to the mixture present in the apparatus, and the mixture was heated to 65°C. The polymerisation was initiated by the addition of 15 ml of a solution of 1 g of sodium formaldehyde sulphonylate and 1 g of sodium bicarbonate in 60 ml of water, and the rest of the solution was added in portions over a period of 3 hours. After polymerisation had started, the remaining vinyl acetate solution and a solution of 30 g of N-methylolacrylamide in 130 ml of water were added to the reaction mixture over a period of 2 hours. When all additions had finished, polymerisation was continued at 70°C for a further hour and the mixture was then cooled. A stable, coarse-particled, coagulate-free dispersion was obtained having a solids content of 50%, and a viscosity of 5500 cP (Epprecht-Rheometer, stage III). Films produced from this dispersion as described in Example 1, gave the following cross-linking values:

50	Untempered film			
	pH	2	4.5	10
	DC	92	0	86
55	Tempered film			
	pH	2	4.5	10
	DC	95	36	85
	S	1.9	3.8	2.8

Example 3

310 ml of water, 23 g of a partially saponified polyvinyl alcohol having a degree

of hydrolysis of 87%, 0.4 g of a sodium alkylarylsulphonate, 0.1 g of calcium chloride, 0.4 g of tartaric acid, and 0.7 g of propionaldehyde were introduced into the apparatus described in Example 1. After rinsing with nitrogen, 65 g of a monomer solution consisting of 400 g of vinyl acetate, 122 g of vinyl laurate, 2 g of an organic hydrogen peroxide, and 5 g of the 2-allylamino-4,6-dichloro-s-s-triazine, were added and the reaction medium was heated to 65°C. The polymerisation was initiated by the addition of 15 ml of a solution of 1 g of sodium formaldehyde sulphonylate and 1 g of sodium hydrogen carbonate in 60 ml of water, and the rest of this solution was added in portions over a period of 3 hours. After the polymerisation had started, the rest of the vinyl acetate solution and a solution of 30 g of the Mannich base of acrylamide with dimethylamine



in 130 ml of water were added to the reaction mixture over a period of 2 hours. When all doses had been added, polymerisation was continued at 65°C for another 30 minutes, and the mixture was then cooled. A coarsely-particulate, stable, coagulate-free polymer dispersion was obtained, which had a viscosity of 4200 cP (Epprecht-Rheometer, stage III) at a solids content of 50%. Films produced from this dispersion as described in Example 1, had the following properties:

90	Untempered film			
	pH	2	4	10
	DC	83	0	75
95	Tempered film			
	pH	2	4	10
	DC	91	54	95
	S	2.2	3.7	3.1

Example 4

420 ml of water, 24 g of nonylphenol etherified with 23 moles of ethylene oxide per mole of nonylphenol, 3 g of a sodium alkylarylsulphonate, 3 g of sodium vinyl sulphonate, 16 g of acrylamide, 2 g of potassium peroxydisulphate, 435 g of diethylhexyl maleate, 165 g of vinyl acetate, and 6 g of 2-allylamino-4,6-dichloro-s-s-triazine were introduced into the apparatus described in Example 1, and the mixture was emulsified with a high-speed stirrer for 5 minutes. The reaction medium was then heated to 65°C, and the polymerisation was started by the addition of 20 ml of a solution of 1.2 g of sodium bisulphate, and 2.3 g of concentrated ammonium in 125 ml of water. The rest of this solution was added in portions over a period of 2 hours. After the poly-

merisation had started, a solution of 30 g of N - methylolacrylamide in 130 ml of water was added over a period of 2.5 hours. When both the additions had been completed, polymerisation was continued for another 1 hour at 70°C, and the mixture was then cooled. A stable, coagulate-free polymer dispersion having particles of an average size was obtained, which was adjusted to a solids content of 50%, with water and then had a viscosity of 1800 cP (Epprecht-Rheometer, stage III). Films produced as described in Example 1 had the following properties:

Untempered film			
pH	2	4	10
DC	57	0	93
Tempered film			
pH	2	4	10
DC	76	65	94

Example 5

350 ml of water, 25 g of isotridecyl alcohol etherified with 20 mole of ethylene oxide per mole of the alcohol, 1 g of sodium alkylsulphonate, 2 g of sodium vinyl sulphamate, and 0.5 g of ammonium peroxydisulphate were introduced into the apparatus described in Example 1. After rinsing with nitrogen, 50 g of a monomer mixture consisting of 450 g of vinyl acetate, 50 g of butyl acrylate, and 10 g of 2 - allylamino - 4,6 - dichloro - s - triazine, were added to the mixture in the apparatus and the reaction medium was heated to 65°C. The polymerisation was initiated by adding 10 ml of a solution of 1 g of sodium metabisulphite and 2 g of sodium bicarbonate in 35 ml of water, and the remainder of this solution was added continuously at the rate of 10 ml per hour. After the polymerisation had started, the remaining monomer mixture and a solution of 20 g of N - methylolacrylamide and 5 g of acrylic acid in 115 ml of water, were added over a period of 2 hours. When all additions had been completed, polymerisation was continued for another 30 minutes at 65°C, and then the mixture was cooled. A coagulate-free, stable dispersion having fine particles was obtained. With a solids content of 50%, the viscosity was 200 cP (Epprecht-Rheometer, stage III). Tempered films were prepared as in Example 1, but at 4 pH values. These films were transparent and highly glossy, and had the following properties:

Tempered film				
pH	2	4	7	10
DC	93	93	92.5	93
S	3.3	3.5	3.8	3.0

Example 6

6 kg of water, 0.25 kg of nonylphenol

etherified with 20 mole of ethylene oxide per mole of nonylphenol, and 20 g of sodium alkylsulphonate were introduced into a 16 litre stirred autoclave equipped with a dosing device and jackets which may be heated or cooled: The mixture was freed from atmospheric oxygen by rising with nitrogen. 500 g of a monomer mixture consisting of 5 kg of vinyl acetate and 100 g of 2 - allylamino - 4,6 - dichloro - s - triazine were then added, heated while stirring to 45°C and brought to a constant pressure of 55 atmospheres gauge using ethylene. Polymerisation was initiated by adding 20 ml of a 0.1% strength palladium sol, of 2 atmospheres gauge of hydrogen and 7 g of ammonium peroxydisulphate in 150 ml of water. At the start of the polymerisation, about 5 minutes after adding the peroxydisulphate, the addition of the remaining monomer mixture and a solution of 200 g of N - methylolacrylamide dissolved in 450 ml of water was started and these two supplies were added continuously over a period of 6 hours. Furthermore, a solution of 25 g of ammonium peroxydisulphate and 4 g of concentrated ammonia in 500 ml of water was added over a period of 8 hours. When all additions were complete, polymerisation was continued for another 1 hour at 45°C and the mixture was then cooled to room temperature and after reducing the pressure to atmospheric pressure, evacuated briefly. A stable, finely particulate, coagulate-free dispersion was obtained. The ethylene content of the polymer was 22%. Films of the dispersion were produced at five different pH values as described in Example 1. These films were transparent, shiny and free of any stickiness after tempering; they exhibited a high degree of flexibility and a high viscosity. They had the following properties:

Tempered film					
pH	2	4	7	9	12
DC	84	84	83	84	84
S	3.0	4.5	4.8	4.5	3.5

Example 7

300 g of water, 60 g of isotridecyl alcohol etherified with 15 mole of ethylene oxide per mole of the alcohol, 5 g of sodium alkylsulphonate, and 0.25 g of sodium vinyl sulphamate were introduced into the apparatus described in Example 1 and heated, while stirring, to 80°C. An emulsion consisting of 530 g of water, 2 g of potassium peroxydisulphate, 1.5 g of sodium alkyl sulphamate, 8 g of acrylic acid, 495 g of methyl methacrylate, 405 g of butyl acrylate, 15 g of N - methylolacrylamide and 18 g of 2 - allylamino - 4,6 - dichloro - s - triazine was added over a period of 2 hours, the reaction temperature being maintained at 80°C. One hour after the monomer emulsion had been

completely added, the mixture was cooled. A stable dispersion free of any coagulate was obtained. Films produced from this dispersion, as described in Example 1, had the following properties:

	Tempered film		
pH	3	7	10
DC	93	95	96.5
S	4.5	4.6	3.7

Example 8

4 kg of water, 100 g of hydroxyethyl-cellulose, 110 g of nonylphenol etherified with 20 mole of ethylene oxide per mole of nonylphenol, and 6 g of sodium alkylarylsulphonate were introduced into a 16 litre stirred autoclave with equipment for dosing and heatable and coolable jackets, and free of atmospheric oxygen by rinsing with nitrogen. A monomer mixture consisting of 2.7 kg of vinyl acetate, 1.3 kg of vinyl laurate, 10 g of *t*-butyl hydroperoxide, 100 g of *N*-methylolacrylamide and 50 g of 2-butenylamino-4,6-dichloro-*s*-triazine was then added while stirring. The contents of the autoclave were then heated to 65°C and brought to a pressure of 3 atmospheres gauge using vinyl chloride. Polymerisation was initiated by commencing the addition of a solution of 6 g of sodium formaldehyde sulfoxylate and 5 g of sodium bicarbonate in 1 litre of water at a rate of about 100 ml per hour and at an inherent temperature of 55°C. Polymerisation was continued for 7 hours at 65°C and for a further 4 hours at 85°C, during which time the vinyl chloride pressure decreased slowly. Finally the mixture was cooled to room temperature and was evacuated briefly. A stable, coagulate-free dispersion was obtained having a viscosity of about 3000 cP at a solids content of 50% (measured with the Epprecht-Rheometer C/II). Film produced from these dispersions, as described in Example 1, had the following properties:

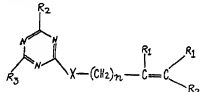
	Untempered film		
Ph	2	4	10
pH	2	4	10
DC	60	0	85
S	4.5	—	4.0

	Tempered film		
pH	2	4	10
DC	70	64	93
S	3.5	4.2	3.0

WHAT WE CLAIM IS:—

1. A copolymer comprising
(i) from 75 to 99% by weight of units derived from one or more monomers selected from vinyl esters, acrylic esters, methacrylic esters, and, optionally, one or more other mono-olefinically or diolefinically unsaturated monomers (excepting those specified under

components (ii) and (iii) below and excepting those specified in claim 13), provided that the weight of units derived from said other monomers does not exceed the weight of units derived from said ester monomers;
(ii) from 0.2 to 15% by weight of units derived from a compound of the general formula—



in which each R₁ denotes a hydrogen atom or methyl group, R₂ denotes a bromine or chlorine atom, R₃ denotes a hydrogen, bromine or chlorine atom, or an alkyl or hydroxy group, X denotes an oxygen or sulphur atom or an —NH— group, and *n* denotes 0, 1, 2 or 3; and

(iii) from 0.2 to 10% by weight of units derived from one or more mono-olefinically unsaturated monomers containing a free or protected *N*-methylol group; all percentages being based on the total weight of components (i), (ii) and (iii).

2. A copolymer as claimed in claim 1, comprising from 90 to 99% by weight of component (i), from 0.5 to 5% by weight of component (ii), and from 0.5 to 8% by weight of component (iii).

3. A copolymer as claimed in claim 1 or claim 2, wherein component (i) comprises units derived from one or more monomers selected from vinyl esters of a carboxylic acid having up to 18 carbon atoms, acrylic esters of a primary or secondary alcohol having up to 18 carbon atoms, and methacrylic esters of a primary or secondary alcohol having up to 18 carbon atoms.

4. A copolymer as claimed in claim 1 or claim 2, wherein component (i) comprises units derived from one or more monomers selected from vinyl esters of a carboxylic acid having 2, 3 or 4 carbon atoms, acrylic esters of a primary or secondary alcohol having up to 8 carbon atoms, and methacrylic esters of a primary or secondary alcohol having up to 8 carbon atoms.

5. A copolymer as claimed in any one of claims 1 to 4, wherein component (i) comprises not more than 50% by weight, relative to the total weight of component (i), of units derived from one or more monomers selected from vinyl halides, vinylidene halides, vinyl aromatic compounds, vinylpyrrolidone, α,β -unsaturated monocarboxylic and/or dicarboxylic acids having from 4 to 10 carbon atoms, esters of the said acids with alcohols having up to 18 carbon atoms, olefins, conjugated diolefins, and acrylonitrile.

6. A copolymer as claimed in any one of claims 1 to 5, wherein component (i) comprises not more than 30% by weight, relative to the total weight of component (i), of units derived from the said other unsaturated monomers.
7. A copolymer as claimed in any one of claims 1 to 6, wherein, in the monomers of component (ii), not more than one R_1 denotes a methyl group.
8. A copolymer as claimed in any one of claims 1 to 7, wherein, in the monomers of component (ii), R_1 denotes a chlorine atom.
9. A copolymer as claimed in any one of claims 1 to 8, wherein, in the monomers of component (ii), R_1 denotes a chlorine atom or a hydroxy group.
10. A copolymer as claimed in any one of claims 1 to 9, wherein, in the monomers of component (ii), X denotes a $-NH-$ group.
11. A copolymer as claimed in any one of claims 1 to 10, wherein, in the monomers of component (ii), n denotes 1 or 2.
12. A copolymer as claimed in any one of claims 1 to 11, wherein component (iii) comprises units derived from one or more monomers selected from N - methylolacrylamide, N - methylolmethacrylamide, N - methylolallylcarbamate, monomers containing an N - methylol alkyl ester group, monomers containing an N - methylol alkyl ether group, and Mannich bases.
13. A copolymer as claimed in any one of claims 1 to 12, additionally comprising (iv) from 0.5 to 10% by weight of units derived from one or more functional olefinically unsaturated monomers (as hereinbefore defined), relative to the total weight of components (i), (ii) and (iii).
14. A copolymer as claimed in claim 13, comprising from 1 to 5% by weight of component (iv), relative to the total weight of components (i), (ii) and (iii).
15. A copolymer as claimed in any one of claims 1 to 14, additionally comprising (v) from 0.05 to 0.5% by weight of triallyl cyanurate or diallyl phosphate, relative to the total weight of components (i), (ii) and (iii).
16. A process for the manufacture of a copolymer as claimed in claim 1, which comprises polymerising monomer components (i), (ii) and (iii) as defined in claim 1 in the presence of a free-radical initiator at a temperature of from 0 to 100°C.
17. A process as claimed in claim 16, carried out in aqueous emulsion in the presence of an emulsifier and/or of a protective colloid.
18. A process as claimed in claim 16 or claim 17, wherein the free-radical initiator is a peroxy compound, optionally in conjunction with a reducing agent.
19. A process as claimed in claim 16, carried out substantially as described in any one of the examples herein.
20. A copolymer as claimed in claim 1, and manufactured by a process as claimed in any one of claims 16 to 19.
21. A process for cross-linking a copolymer as claimed in any one of claims 1 to 15 and 20, which comprises heating it to a temperature of from 100 to 150°C.
22. A process for cross-linking a copolymer as claimed in any one of claims 1 to 15 and 20, which comprises heating it to a temperature of from 130 to 150°C.
23. A process for cross-linking a copolymer as claimed in any one of claims 1 to 15 and 20, which comprises treating it with an acid catalyst at a pH below 3.
24. A process for cross-linking a copolymer as claimed in any one of claims 1 to 15 and 20, which comprises treating it with a basic catalyst at a pH above 9.
25. A cross-linked copolymer manufactured by a process as claimed in any one of claims 21 to 24.

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